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Proceeding Paper

Predictive Evaluation of Atomic Layer Deposition Characteristics for Synthesis of Al_2O_3 thin films†

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Abstract: Atomic Layer Deposition (ALD) synthesis process is being heavily researched for it conformality, high aspect ratio with thickness control, selective area deposition versatility, variety of low temperature oxide, nitride, and transition metal dichalcogenides (TMDC)precursors for multitude of applications. Repeatability and reproducibility are essential along with large scale deposition with high throughput from commercialization perspective of ALD thin films from new precursors. JMP and Design of Experiment (DoE) are industrially practiced tools to study and reduce variations in the processes. Reducing variations improves repeatability. This research demonstrates the application of DoE with JMP to study variation of ALD synthesis of Al_2O_3 and improve predictability.

Keywords: Atomic Layer Deposition (ALD); Transition Metal Dichalcogenides (TMDC); Design of Experiment (DoE); Repeatability; Reproducibility, Predictability

Introduction: Atomic Layer Deposition (ALD) is the variant of chemical vapor deposition where the reactants are supplied sequentially as a timed pulse. The pulse of reactant precursor is usually separated by purging step of inert gas pulse or having intermittent purge time. The precursors introduced to the ALD chamber chemisorb in a self-limiting manner. Chemisorption of precursor is reactive site dependent and thus provides very precise thickness control over intricate surfaces with high conformality and aspect ratio [1]. These aspects of atomically controlled thickness due to self-limiting reaction mechanisms with high conformality and ease of operation has made ALD the most prospective deposition technique for semiconductor and synthetic biological applications. The research gap that there is a lack of emphasis on the repeatability studies related to the new synthesis processes like ALD has been identified. There is need of research and evaluation of ALD process using DoE to establish repeatability and reproducibility of the new 2D thin films being synthesized. One factor at a time (OFAT) experimentation is still the highly relied strategy during research for understanding the cause – effect relationship [2]. The serious drawback of OFAT experimentation strategy lies in the fact that, engineering processes invariably interact. Significant research efforts are devoted to understanding the underlying phenomenological aspects using density functional theory (DFT) and molecular dynamics (MD) simulations [3,4]. At nanoscale, the parametric interactions have significant effect and thus necessitates the usage of experimentation strategy like DoE. Gauge repeatability and reproducibility, Monte Carlo Simulations when integrated with DoE provide a dependable means to evaluated and predict performance of the processes. The simple but effective DoE analysis may aid the DFT/MD results to make the new processes and product development more predictive and sustainable. Thus, this research attempts to acquaint the reader with the ALD synthesis of Al_2O_3 thin films. Further the effect of input parameters of ALD such as pulse duration of precursor, temperature on the output response of thickness and stoichiometry of the Al_2O_3 thin films synthesized is studied. The effectiveness of the DoE with JMP has been explained with note on ease of usage of Monte-Carlo Simulation for predictive evaluation. For the first time the simultaneous pulsing of Ozone and H_2O pulse is evaluated using DoE. Significantly high deposition rate of Al_2O_3 is observed.

Materials and Methods: The accompanying schematic of ALD in Figure 1 is for Vecco Savannah Thermal S200 ALD system. It has four cannisters for Ozone (O_3), Trimethyl Aluminum (TMA), Cobalt (Co) and Water (H_2O). The ALD precursors having suitable vapor pressure were procured from Strem Chemicals. It is imperative to know the vapor pressure of the precursor at various temperature or else, the cannisters is heated to increase vapor pressure. The volatility due to vapor pressure of the precursors is critical for the chemisorption [5,6]. The Swagelok cylinders are connected to a manifold that provides independent path for each precursor to the ALD chamber. Solenoid valves control the amount of precursor pulse based on the valve timing. The 6″ or 8″ Silicon (1,0,0) wafer with a layer of 300 nm SiO_2 is procured from University Wafers. Before deposition of Al_2O_3, the substrate is cleaned with IPA, rinse with DI water and dried with N_2. Figure 2. demonstrates the ALD recipe that has instructions, channel with units for process parameters.

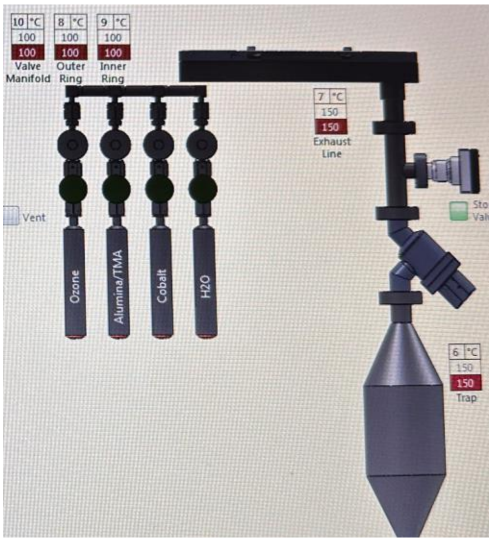
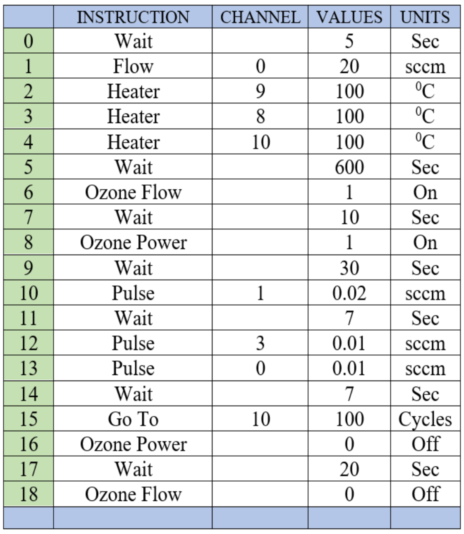


Figure 1. Schematic of Vecco Savvanah ALD.



	INSTRUCTION	CHANNEL	VALUES	UNITS
0	Wait		5	Sec
1	Flow	0	20	sccm
2	Heater	9	100	^{0}C
3	Heater	8	100	^{0}C
4	Heater	10	100	^{0}C
5	Wait		600	Sec
6	Ozone Flow		1	On
7	Wait		10	Sec
8	Ozone Power		1	On
9	Wait		30	Sec
10	Pulse	1	0.02	sccm
11	Wait		7	Sec
12	Pulse	3	0.01	sccm
13	Pulse	0	0.01	sccm
14	Wait		7	Sec
15	Go To	10	100	Cycles
16	Ozone Power		0	Off
17	Wait		20	Sec
18	Ozone Flow		0	Off

Figure 2. Vecco ALD Recipe for Al_2O_3

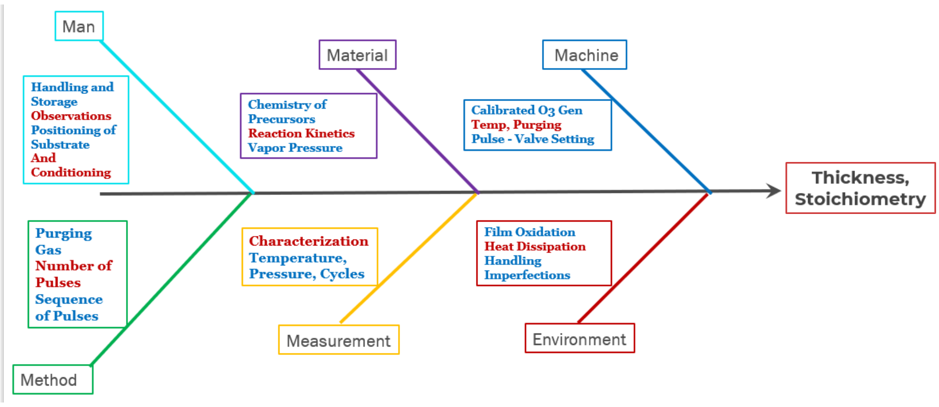


Figure 3. Ishikawa Diagram for ALD Factors

The steps of recipe in Figure 2. are self-explanatory; however, the deposition characteristics are modified by the order and time of the precursor supply, temperature, purging

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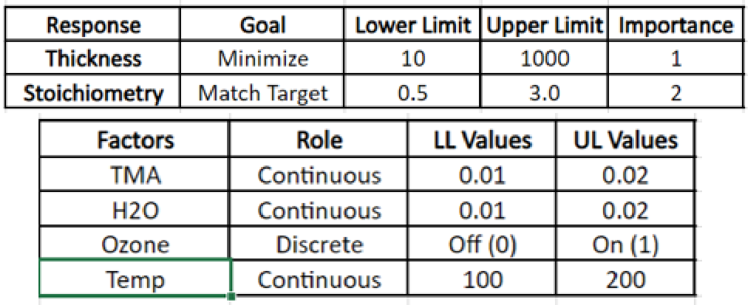
time, number of cycles. For determination of parameters and responses to be studied during experimentation by designing, it is very important to list and identify several parameters and responses (factors)associated with ALD process in an Ishikawa diagram as shown in Figure 3.

From the practical perspective, the effectiveness of the DoE model depends on the sensitivity analysis of the process input factors. The sensitivity analysis of the input parameters means weather the limits chosen to vary is causing a significant impact on the response characteristics of interest. Considering the linear relationship of number of pulses and thickness of the deposition, during this exercise, number of cycles were kept constant. DoE is effective only if carefully designed with significant engineering insight and experience of the parameters. Once effectively designed, there are numerous major benefits of DoE from manufacturing perspective.

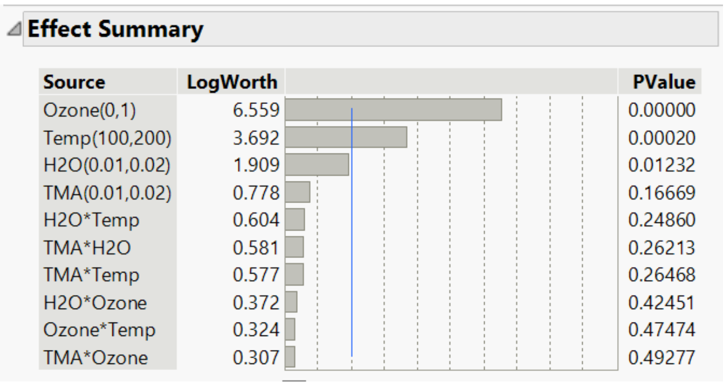
Results and Discussion: While new ALD variants and material chemistries are developed, consistency and reproducibility is required to be addressed [7,8]. JMP tool is an industry standard for DoE. The "Custom Design" utility in JMP-DoE menu equips users with an intuitive DoE model development. First the response characteristics are to be defined. The definition of response characteristics includes the name as identifier, the targeted response as to minimize, maximize or match the target. Like, for Al_2O_3 layer thickness is to be minimized optimally without compromising refractive index (IR) or density. If IR or density is chosen as response characteristics, it is the property of the material so that it has to be matched as close to the expected value as possible. For the DoE of Al_2O_3, the stoichiometric response is to be matched in the ration of 2:3. Once the response characteristics are amicably defined, the input parameters identified as factors are defined with naming identifier and lower (-1) and upper (+1) limits of the parameter. The factors identified for v Al_2O_3 synthesis are TMA pulse of 0.01 to 0.02 sec, H2O pulse of 0.01 to 0.02 sec, Ozone pulse On/Off and temperature of 100 to 200 ^{0}C. When On, the Ozone pulse will be for 0.01 sec. Out of the several types of model design available in JMP, response surface methodology (RSM) is chosen. Based on the number and types of responses and factors, the DoE table is derived. The effects table of Figure 5. conclusively identifies that ozone is the most dominant factor for the chosen responses.



Response	Goal	Lower Limit	Upper Limit	Importance
Thickness	Minimize	10	1000	1
Stoichiometry	Match Target	0.5	3.0	2

Factors	Role	LL Values	UL Values
TMA	Continuous	0.01	0.02
H2O	Continuous	0.01	0.02
Ozone	Discrete	Off (0)	On (1)
Temp	Continuous	100	200

Figure 4. ALD Factors and Responses for DoE

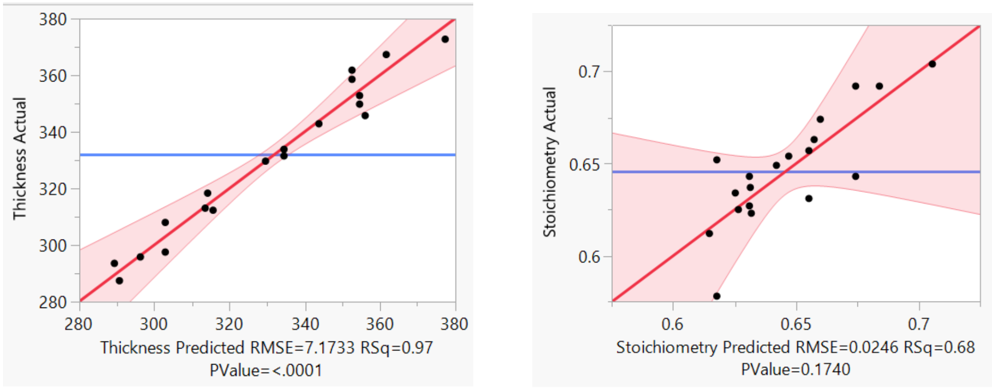


Effect Summary

Source	LogWorth	PValue
Ozone(0,1)	6.559	0.00000
Temp(100,200)	3.692	0.00020
H2O(0.01,0.02)	1.909	0.01232
TMA(0.01,0.02)	0.778	0.16669
H2O*Temp	0.604	0.24860
TMA*H2O	0.581	0.26213
TMA*Temp	0.577	0.26468
H2O*Ozone	0.372	0.42451
Ozone*Temp	0.324	0.47474
TMA*Ozone	0.307	0.49277

Figure 5. ALD Parametric Effects and Interaction Summary

The effects table has conclusively identified that ozone is the most dominant factor for the chosen responses. Temperature is the second most influential factor. Subsequently, all other individual factor is not dominant, but interaction of the factors is statistically significant. One important question arises here, in what manner the dominant factors are influencing the response? This requires an insight into the setting up of the DoE. As there are two response parameters chosen for analysis, these factors can be dominant with any one or both. Furthermore, the response characteristics for thickness was to minimize and for stoichiometry was "match target", thus the effects table is pointing to this desirability defined during the construction of DoE.



(a) **(b)**

Figure 6. Plots for Actual vs. Predicted values of (**a**) Thickness and (**b**) Stoichiometry.

The plots of actual vs predicted values of response characteristics to be interpreted depends upon the expectations set during the construction of DoE. The narrow plot for thickness means that there is good agreement in the actual vs predicted value and the design is significantly aligns with the targeted response. This validates the design and construction of the DoE. It can be inferred that that DoE model is developed to predict thickness in more accurate manner. But conversely, the model has large scatter in the stoichiometric ratios of the Al_2O_3 deposited. Thus, the assumptions made during DoE construction with reference to the stoichiometry were not reasonable or the XPS analysis of the ALD Al_2O_3 needs to be refined. If the DoE model constructed is significant the factors can be determined from the model to obtain the targeted output. Thus, Figure 7 is the optimized targeted response where stoichiometry too of 0.65 is achieved.

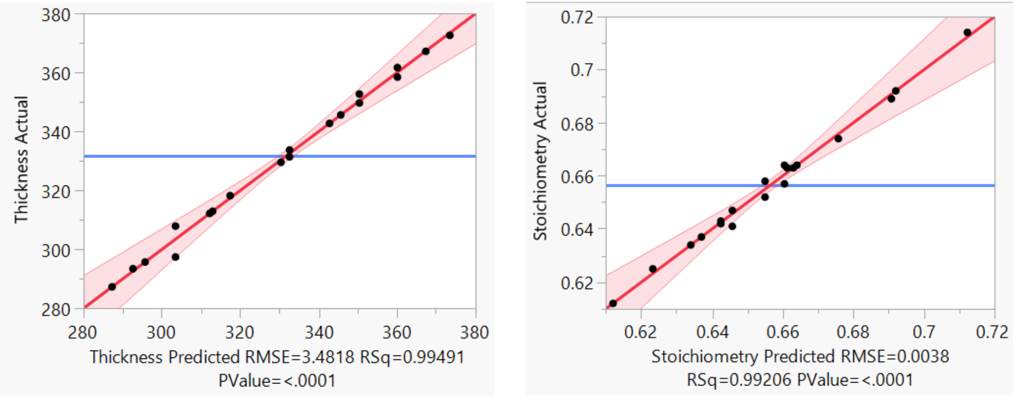
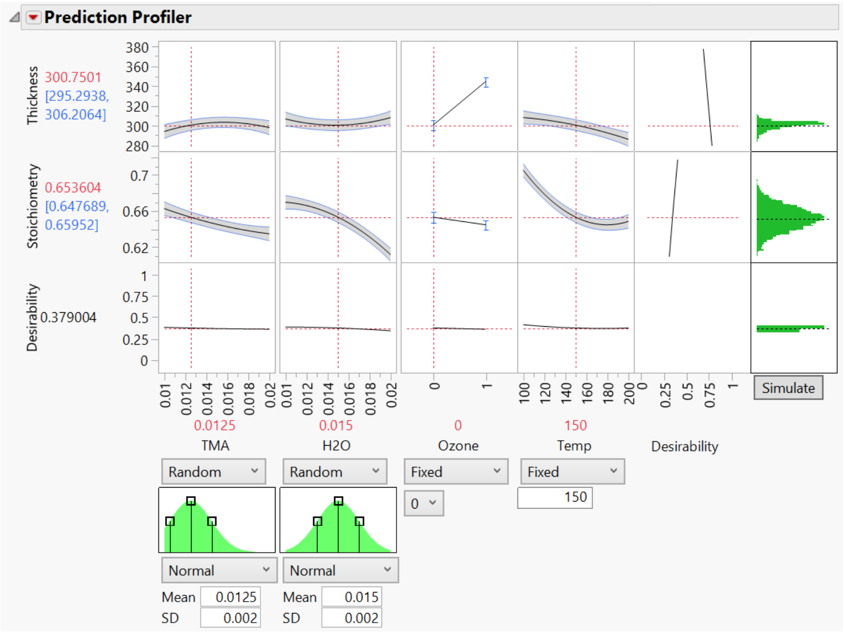


Figure 7. Optimized Thickness and Stoichiometry Plots

The most efficient feature of the DoE with the JMP is this desirability plot for the achieving the targeted response. From the predictor profiler of Figure 8, the engineers and scientists can choose the values of the factors to achieve best combination of desirability.

The red line vary high for thickness at 300 A and at around 0.65 for stoichiometry. To achieve these response conditions the factors required are TMA pulse of 0.0125, H_2O pulse of 0.015, Ozone OFF and Temperature of 150 0C. If the limits of random variations in the ALD process for TMA and H_2O pulse are known, the Monte-Carlo simulation has capability to provide distribution of response which can be further used to determine the defective parts per million as well for the specified variability of the ALD process.



TMA: Random, Normal, Mean 0.0125, SD 0.002

H2O: Random, Normal, Mean 0.015, SD 0.002

Ozone: Fixed, 0

Temp: Fixed, 150

Figure 8. Predictor Profiler with Monte-Carlo Simulator for the Optimized Factors

Researchers can improve understanding and evaluate the process design strategy and build repeatability using utilities in JMP [9].

Conclusion: The synthesis of Al_2O_3 with ALD has successfully resulted into predictive DoE model development. The influence of the Ozone is based on the reaction kinetics. Ozone has suitable energetics for ligand removal as well as exchange to form Al_2O_3 from TMA. The removal of Ozone during the purging cycle is also responsible for the conformal Al_2O_3 deposition. The dual pulse of H_2O and Ozone has resulted into a combination reaction causing an abruptly high GPC of about 3 A/cycle. The DoE predictor profiler and model was useful to determine optimized input factors to achieve targeted response. Thus, in conclusion it can be inferred that the ALD recipe development along with use of JMP tools are effective for developing a predictive DoE model.

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The authors declare no competing financial interests.

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